

Ionic liquids as solvents of polar and non-polar solutes: affinity and coordination. Supplementary Information.

Elixabete Rezabal^{*,†} and Thomas Schäfer^{*,‡,§}

Laboratoire de Chimie Moléculaire, Department of Chemistry, Ecole Polytechnique and CNRS, 91128 Palaiseau Cedex, France, POLYMAT, University of the Basque Country UPV/EHU 20018 Donostia-San Sebastián, Spain, and IKERBASQUE, Basque Foundation for Science, Bilbao, Spain

E-mail: elixabete.rezabal@polytechnique.edu; thomas.schafer@ehu.es

Technical parameters of ab initio molecular dynamics (AIMD) calculations

The initial geometries for the AIMDs were extracted from classical MD simulations carried out employing the GROMACS¹⁻⁴ package. A cubic box of 82 Å length containing 3002 [MIM][Cl] ion pairs and a H₂O or CO₂ molecule was generated and temperature increased using velocity rescaling, first with a timestep of 0.02 fs during 100ps and afterwards with 0.2 fs during 50 ps. Posteriorly, it was equilibrated in NPT ensemble at 1 bar and 425 K to converge the system towards the experimental density of 1.174 g/cm at 425K.⁵ A timestep of 0.5 fs was used, during 1 ns (Parrinello isostat, Nose-Hoover thermostat).

*To whom correspondence should be addressed

[†]Laboratoire de Chimie Moléculaire, Department of Chemistry, Ecole Polytechnique and CNRS, 91128 Palaiseau Cedex, France

[‡]POLYMAT, University of the Basque Country UPV/EHU 20018 Donostia-San Sebastián, Spain

[§]IKERBASQUE, Basque Foundation for Science, Bilbao, Spain

A box of 18 [MIM][Cl] ion pairs with the solute in the center was extracted from the classical MD equilibrated system and simulated by applying periodic boundary conditions with a box length of 15x15x15 Å. Ab initio molecular dynamics (AIMD) simulations were based on the Car-Parrinello method⁶ and were performed with the CPMD code.⁷ The general gradient-corrected density functional BLYP with empirical dispersion correction⁸ was chosen and the Kohn-Sham orbitals were expanded in a plane wave basis with a kinetic energy cutoff of 70 Ry. A fictional electron mass of 400 a.u. and a time step of 4.0 a.u. were used throughout all CPMD simulations. The temperature was set to 425K, initially controlled by velocity rescaling and after by Nose-Hoover chain thermostats.⁹⁻¹¹ The equilibration period was carried with Nose-Hoover chain thermostats coupled to each ionic degree of freedom, and subsequently the system was relaxed applying thermostats. Finally, the system was simulated in NVT ensemble, reaching a production time of around 33ps.

Geometrical parameters of CO₂-([MIM][Cl])_n and H₂O-([MIM][Cl])_n (n=1,2) complexes

Table 1: Geometrical parameters of H₂O-[MIM][Cl] isomers, at BLYP-D/TZVP theory level, angle in degrees and distances in Å.

		H _w -O-H _w	H _w -O	H _w -Cl	H _r -Cl	H _r -O	H _{met} -O	
Gas phase	1	104.7	1.004	0.972	2.113	2.818	2.172	2.439
	2	103.9	1.003	0.972	2.122	2.183	2.887	2.355
	3	103.9	1.004	0.972	2.167	2.167	2.672	2.150
IL phase	1	104.1	1.002	0.975	2.119	3.262	2.228	2.646
	2	103.9	0.996	0.975	2.175	2.440	2.791	3.299
	3	103.7	0.998	0.975	2.146	2.492	2.782	2.366

Table 2: Geometrical parameters of $\text{H}_2\text{O}([\text{MIM}][\text{Cl}])_2$ complexes, at BLYP-D/TZVP theory level, angle in degrees and distances in Å.

	$\text{H}_w\text{-O-H}_w$	$\text{H}_w\text{-O}$	$\text{H}_w\text{-Cl}$	$\text{H}_r\text{-Cl}$	$\text{H}_r\text{-O}$	$\text{H}_{Met}\text{-O}$				
Gas phase 1	104.5	0.991	2.259	2.311	2.273	2.351	3.387	3.077	2.475	2.512
2	104.5	0.990	2.311	2.258	2.271	2.354	3.380	3.085	2.475	2.515
3	103.4	0.990	2.218	2.266	2.410		2.642	3.273	2.253	2.497
4	104.1	0.995	2.309	2.232	2.385		3.362	3.183	2.535	2.444
5	104.8	0.994	2.258	2.351	2.428		3.521	3.526	2.572	2.599
IL phase 1	105.8	0.993	2.223	2.269	2.542		2.919	2.804	2.899	3.835
2	103.5	0.998	2.150		2.794	2.497	2.489		2.423	
3	106.0	0.993	2.315	2.217	2.509		3.179	3.073	3.088	
4	106.0	0.993	2.217	2.315	2.509		3.179	3.073	3.088	
5	104.9	0.993	2.210	2.296	2.503		3.095	3.097	2.994	3.006

Table 3: Geometrical parameters of CO₂-[MIM][Cl] isomers, at BLYP-D/TZVP theory level, angle in degrees and distances in Å.

		O-C-O	C-O	C-Cl	H _r -Cl	H _r -C	H _r -O	H _{Met} -O	
Gas phase	1	174.4	1.170	1.181	3.136	2.707	3.100	2.357	2.803
	2	173.7	1.171	1.181	3.119	2.038	3.375	2.889	2.716
	3	173.6	1.176	1.175	3.143	2.149	3.540	3.767	2.608(3.060)
IL phase	1	175.1	1.173	1.176	3.197	2.960	3.099	2.448	3.070
	2	175.9	1.173	1.175	3.242	2.305	3.300	2.741	2.943
	3	176.0	1.174	1.174	3.276	2.558	3.463	3.372	2.963(3.216)

Table 4: Geometrical parameters of $\text{CO}_2\text{-}([\text{MIM}][\text{Cl}])_2$ isomers, at BLYP-D/TZVP theory level, angle in degrees and distances in Å.

	O-C-O	C-O	C-Cl	H _r -Cl	H _r -C	H _r -O	H _{Met} -O				
Gas phase 1	175.2	1.174	3.292	2.464	2.459	2.989	2.994	2.584	2.590	2.497	2.493
2	175.1	1.173	1.177	3.189	2.335	2.263	2.918	2.927		2.611	
3	173.6	1.175	1.176	3.134	2.234	2.428	3.759	3.251		2.701	
4	175.1	1.177	1.173	3.188	2.262	2.335	2.918	2.925		2.608	
5	171.6	1.177	1.176	3.045	2.258			3.092	2.542	2.559	
IL phase 1	176.6	1.174	1.174	3.299	2.329	2.345	2.954	3.200		3.092	
2	174.9	1.175	1.174	3.176	2.347	2.488	3.463	3.254		2.720	
3	175.7	1.175	1.173	3.220	2.406	2.417	2.998	3.245		2.669	3.074
4	175.1	1.174	1.174	3.201	2.455			3.879		3.089	
5	176.5	1.174	1.174	3.305	2.455					2.794	2.804

Topological analysis

The NCI method is based on the relationship of the reduced density gradient (s) and the electron density (ρ):¹²

$$s = \frac{1}{2(3\pi^2)^{\frac{1}{3}}} \frac{|\nabla\rho|}{\rho^{\frac{4}{3}}} \quad (1)$$

The representation of s versus ρ shows characteristic peaks at low density values in the presence of non-covalent interactions due to the annihilation of the density gradient at these points. On one hand, the strength of the interaction is derived from the density values of the low-gradient spikes. Dispersion interactions usually appear at very low density values ($\rho < 0.01$ a.u.), whereas stronger hydrogen-bonds appear at higher density values ($0.01 < \rho < 0.05$ a.u.). On the other hand, the sign of the second eigenvalue (λ_2) of the electron-density Hessian matrix is used to distinguish between bonded ($\lambda_2 < 0$) and non-bonded ($\lambda_2 > 0$) interactions. Since the sign of the second eigenvalue [$\text{sign}(\lambda_2)$] is indicative for the type of interaction, the gradient is plotted against the product of the $\text{sign}(\lambda_2)$ and the electron density function. A very important tool is the visualization of the gradient isosurface in real space (3D plots). Again, the value of the $\text{sign}(\lambda_2)\rho$ is used to colour the different isosurfaces. Usually, a RGB (red-blue-green) scale is used; red isosurfaces indicate repulsive interactions, blue stands for attractive interactions and green for very weak van der Waals-type interactions.

NCI analysis of $\text{H}_2\text{O}([\text{MIM}][\text{Cl}])$ and $\text{CO}_2([\text{MIM}][\text{Cl}])$ complexes

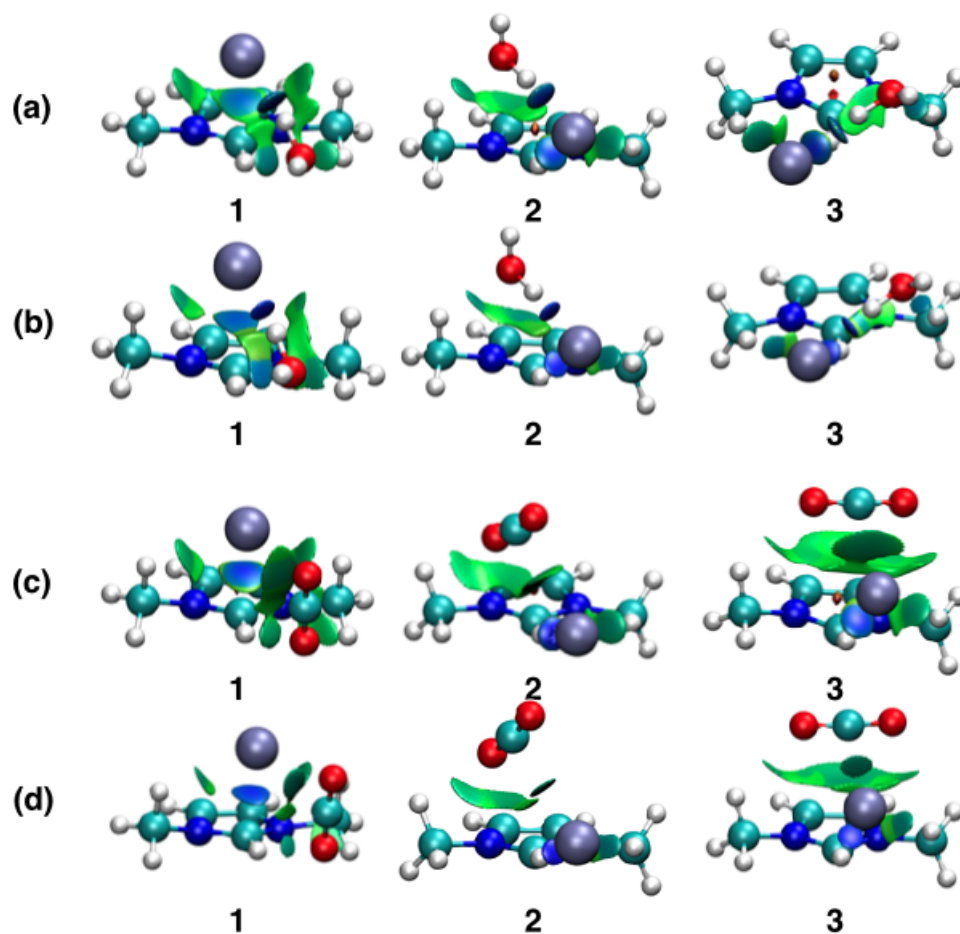


Figure 1: 3D plot of $\text{sign}(\lambda_2)\rho$ ($s=5.0$ a.u.) for the different $\text{H}_2\text{O}([\text{MIM}][\text{Cl}])$ ((a) and (b)) and $\text{CO}_2([\text{MIM}][\text{Cl}])$ ((c) and (d)) isomers using wave function ((a) and (c)) and promolecular ((b) and (d)) densities for the NCI analysis.

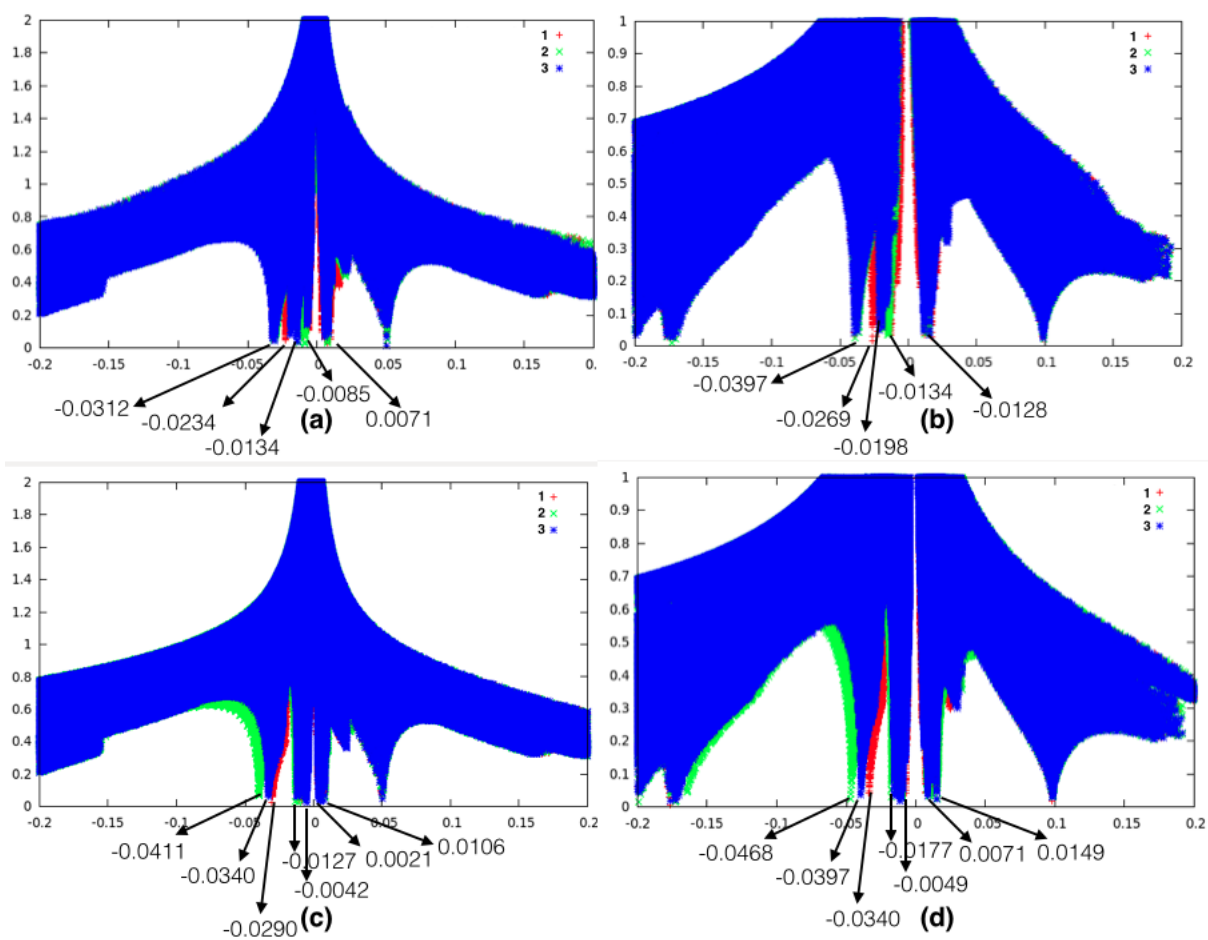


Figure 2: 2D plot of $\text{sign}(\lambda_2)\rho$ for the different H₂O([MIM][Cl]) ((a) and (b)) and CO₂([MIM][Cl]) ((c) and (d)) isomers using wave function ((a) and (c)) and promolecular ((b) and (d)) densities for the NCI analysis. $\text{sign}(\lambda_2)\rho$ values are noted for the peaks of interest, in order to facilitate the comparison between pro molecular and wave function density analyses.

Additional radial distribution functions (RDFs) for the Sol- [MIM][Cl]₁₈ systems

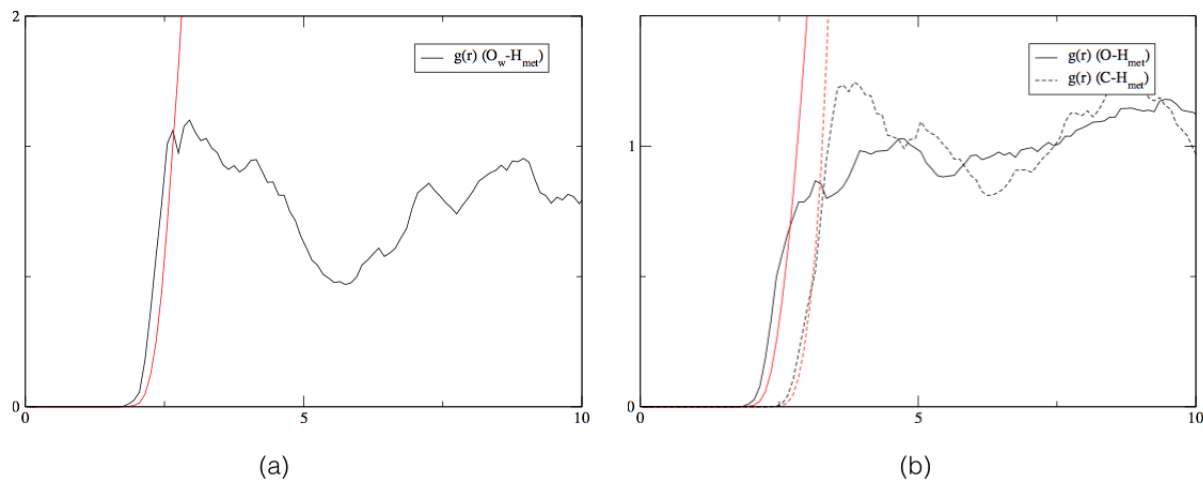


Figure 3: (a) $\text{O}_w\text{-H}_{met}$ RDFs (black line) and the corresponding integral (red line) in the H_2O -[MIM][Cl]₁₈ system. (b) O-H_{met} (solid line) and C-H_{met} (dashed line) RDFs (black lines) and the corresponding integral (red lines) in the CO_2 -[MIM][Cl]₁₈ system. The distance between the atoms (x axis) is in Å.

Affinity energies Sol-[MIM][Cl]₁₈ systems

Table 5: Affinity (ΔE) and dispersion (ΔE_{disp}) energies of Sol-([MIM][Cl])₁₈ systems, at BLYP-D(SMD)/TZVP theory level, in kcal/mol.

	H ₂ O		CO ₂	
	ΔE	ΔE_{disp}	ΔE	ΔE_{disp}
1	-8.4	-8.9	-7.6	-10.0
2	-10.7	-7.1	-3.5	-10.6
3	-13.3	-7.3	-4.6	-11.4
4	-16.3	-7.8	-7.3	-12.4
5	-9.5	-2.8	-5.3	-9.9
6	-14.7	-8.3	-6.5	-9.8
7	-12.3	-9.0	-10.0	-11.5
8	-14.7	-12.0	-6.3	-11.3
9	-14.5	-7.0	-7.6	-11.0
10	-11.9	-9.9	-10.0	-14.0
11	-12.8	-8.5	-6.3	-9.1
12	-12.2	-8.3	-5.6	-11.2
13	-10.6	-6.7	-8.3	-10.8
14	-12.7	-8.2	-7.1	-9.7

SMD input example for the IL phase

```
%mem=7520mb
%nprocshared=8
%chk=cmimcl.chk
#m06/TZVP gfinput opt freq scrf=(smd,solvent=generic)
```

DBAphenyl F Scan

0 1

C -1.890058 -1.487067 1.527614

N -2.164846 -0.274264 2.115251

C -1.106831 0.107610 2.817863

C -0.153261 -0.808607 2.683183

N -0.630339 -1.823034 1.884513
C -3.463567 0.376668 2.147877
H 0.723397 -0.816752 3.164228
O -2.686067 -1.906209 4.615484
C -5.330680 -2.487563 4.340238
O -5.478797 -2.720272 5.463685
O -5.255630 -2.325065 3.199574
O -5.282950 0.198427 4.934652
C -3.288660 -2.878548 7.594465
N -2.123154 -3.486075 7.411071
C -1.123175 -2.545779 7.506811
C -1.716970 -1.358180 7.770215
N -3.072379 -1.590266 7.826709
C -1.937545 -4.891401 7.027998
C -2.875411 -5.305265 5.915297
C -2.482479 -6.654613 5.343929
C -3.386570 -7.065145 4.199659
C -4.103163 -0.578357 8.009476
Cl -2.361963 1.202032 5.592618
Cl 0.015820 -3.689615 4.602305
H -2.466140 -1.022841 4.959557
H -1.851693 -2.417364 4.595078
H -2.634798 -2.016994 0.959060
C 0.139454 -3.018619 1.657368
H -1.092792 0.966283 3.476957
H -4.194075 -0.318518 2.561982
H -3.398943 1.238304 2.811451
C -3.844708 0.791307 0.811724
H -1.319407 -0.358947 7.840217

H -0.099103 -2.800803 7.284843
H -4.306751 -0.434984 9.071196
H -5.002467 -0.895399 7.482191
H -3.745206 0.347154 7.551659
H -4.258034 -3.341689 7.524364
H -0.910002 -4.961511 6.663789
H -2.054627 -5.516980 7.918345
H -3.915599 -5.335544 6.266901
H -2.819710 -4.548463 5.125647
H -1.446089 -6.586823 4.994305
H -3.100792 -8.032686 3.782940
H -4.430056 -7.136489 4.521468
H -3.339630 -6.328896 3.392436
H -2.501060 -7.416603 6.133611
H -4.399400 0.570682 5.132802
H -5.877232 0.949299 4.968225
C -5.141250 1.438869 0.858003
H -3.104236 1.488832 0.423031
H -3.897681 -0.081151 0.162161
C -5.522390 1.853508 -0.478151
H -5.881721 0.741344 1.246695
H -5.088276 2.311328 1.507565
H -6.496138 2.339850 -0.443393
H -4.781919 2.551033 -0.866843
H -5.575364 0.981050 -1.127713
H -0.415083 -3.688300 1.001671
H 1.087785 -2.756546 1.190563
H 0.327815 -3.515173 2.608092

eps=11.5 epsinf=2.0449 HBondAcidity=0.229 HBondBasicity=0.265
SurfaceTensionAtInterface=61.24 CarbonAromaticity=0.375
ElectronegativeHalogenicity=0.125

References

- (1) Berendsen, H.; van der Spoel, D.; van Drunen, R. *Comput. Phys. Commun.* **1995**, *91*, 43–56.
- (2) Lindahl, E.; Hess, B.; van der Spoel, D. *Molecular modeling annual* **2001**, *7*, 306–317.
- (3) Van Der Spoel, D.; Lindahl, E.; Hess, B.; Groenhof, G.; Mark, A. E.; Berendsen, H. J. C. *J. Comput. Chem.* **2005**, *26*, 1701–1718.
- (4) Hess, B.; Kutzner, C.; van der Spoel, D.; Lindahl, E. *J. Chem. Theory Comput.* **2008**, *4*, 435–447.
- (5) Fannin, A. A.; Floreani, D. A.; King, L. A.; Landers, J. S.; Piersma, B. J.; Stech, D. J.; Vaughn, R. L.; Wilkes, J. S.; L., W. J. *J. Phys. Chem* **1984**, *88*, 2614–2621.
- (6) Car, R.; Parrinello, M. *Phys. Rev. Lett.* **1985**, *55*, 2471–2474.
- (7) CPMD, Copyright IBM Corp 1990-2006, Copyright MPI fur Festkorperforschung Stuttgart 1997-2001.
- (8) Grimme, S. *J. Comput. Chem.* **2006**, *16*, 1787.
- (9) Nose, S. *J. Chem. Phys.* **1984**, *81*, 511–519.
- (10) Nose, S. *Mol. Phys.* **1984**, *52*, 255–268.
- (11) Hoover, W. *Phys. Rev. A* **1985**, *31*, 1695–1697.
- (12) Johnson, E. R.; Keinan, S.; Mori-Sanchez, P.; Contreras-Garcia, J.; Cohen, A. J.; Yang, W. *J. Am. Chem. Soc.* **2010**, *132*, 6498–6506.